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Relaxation Effects in the Transport Properties of a Gas of Rough Spheres*

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The rough-sphere model is investigated in some detail from the point of view of the formal kinetic theory of polyatomic molecules developed by Wang Chang and Uhlenbeck, and by Taxman. The purpose is to clarify the sources of some discrepancies between the known results for the transport properties of a rough-sphere gas and the results recently obtained by Mason and Monchick in an approximate treatment of the formal kinetic theory, in which the corrections for inelastic collisions are given in terms of relaxation times. It is found that the deviations of the transport coefficients of rough spheres from those of smooth spheres can be understood in first approximation as the result of two effects: an enhancement of the backward and side-ward scattering of rough spheres over that for smooth spheres, and an apparent resonant exchange of internal energy when two rough spheres collide. Since these effects are, for the most part, peculiar to rough spheres, it is concluded that the deviations found between the rough-sphere model and the approximate theory are not to be expected for real molecules.

I. INTRODUCTION

A FORMAL kinetic theory of gases which takes into account inelastic collisions has been developed by Wang Chang and Uhlenbeck¹ for the semi-classical case and by Taxman² for the classical case as an extension of the Chapman-Enskog kinetic theory.^{3,4} In its original form the Chapman-Enskog theory is strictly applicable only to the noble gases. The new formal theory should therefore be much more applicable to most gases, but the expressions for the transport coefficients derived from this formal theory are complicated and the integrals involved appear almost hopelessly difficult, since they require a solution of the dynamical problem of inelastic molecular collisions. Recently a tractable approximation to the formal theory has been proposed by Mason and Monchick,⁵ who argued that certain terms in the expressions are small and can be neglected, and who then were able to avoid an explicit evaluation of the remaining integrals by expressing them in terms of an experimental quantity, the relaxation time, or bulk viscosity. That is, the

difficult integrals were evaluated by appeal to experiment rather than to a computer, at least to a first-order correction for the inelastic collisions (relaxation times).

There are two customary ways of checking such an approximate theory: by comparison with experiment, and by comparison with some special model for which accurate theoretical calculations can be carried out. As far as comparison with experiment was possible, the approximate theory checked satisfactorily,⁵ although the comparison was limited by a scarcity of data on rotational relaxation times. For comparison with a solvable theoretical model, the rough-sphere gas was used. Here the approximate theory was partly in good agreement with the rough-sphere model, but gave a notable discrepancy in that part of the coefficient of thermal conductivity due to the molecular internal degrees of freedom. To first order, the translational heat conductivity was given exactly and the shear viscosity fairly accurately. We have since found another large discrepancy in the self-diffusion coefficient. These discrepancies might be due either to some fundamental fault in the approximate theory, or to the physically unrealistic nature of the rough-sphere model, which has some features not found in real molecules. The latter cause is suggested by the agreement of the approximate theory with the experimental thermal conductivities of polyatomic and polar gases, but the point seemed worthy of further investigation.

It is the purpose of this paper to investigate the rough-sphere model in more detail from the point of view of the formal kinetic theory, and of its more approximate version proposed by Mason and Monchick, with the aim of clarifying the sources of the above mentioned discrepancies. The exact results for the rough-sphere

* This work was supported in part by the Bureau of Naval Weapons, Department of the Navy, and in part by the National Aeronautics and Space Administration.

¹ C. S. Wang Chang and G. E. Uhlenbeck, "Transport Phenomena in Polyatomic Gases," University of Michigan Engineering Research Rept. No. CM-681, July 1951. See also reference 4, pp. 501-506.

² N. Taxman, Phys. Rev. **110**, 1235 (1958).

³ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1952), 2nd ed.

⁴ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

⁵ E. A. Mason and L. Monchick, J. Chem. Phys. **36**, 1622 (1962).

model have been known for some time: the shear viscosity and the two thermal conductivity coefficients (translational and internal) were calculated by Pidduck,^{6,7} the diffusion coefficient by Chapman and Cowling,⁷ and the relaxation time (or bulk viscosity) by Kohler⁸ and by Wang Chang and Uhlenbeck.¹ We have nothing new to add to these results; we offer only some physical interpretations and analogies which we believe useful and which we believe point to the special peculiarities of the model as the source of the discrepancies rather than to a fundamental defect of the approximate theory.

A few remarks on the rough-sphere model may be made here. By "rough" it is meant that when two spheres collide their surfaces grip without slipping and the relative velocity of the points of contact reverses.^{6,7} The deviations of the rough-sphere results from the smooth-sphere results are usually given in terms of a dimensionless parameter, K , defined as $K = 4I/m\sigma^2$ where I is the moment of inertia of the sphere; m , its mass; and σ , its diameter. K ranges from 0 to $\frac{2}{3}$. We will usually work only to first order in K , since the approximate theory gives only first-order corrections. To this order, the exact expressions for the viscosity η , the self-diffusion coefficient D_{11} , the two thermal conduction coefficients λ_{tr} and λ_{int} , and the relaxation time τ are

$$\eta = \frac{5}{16}[(\pi mkT)^{1/2}/(\pi\sigma^2)](1 - \frac{1}{6}K + \dots), \quad (1a)$$

$$D_{11} = \frac{3}{8}[(\pi mkT)^{1/2}/(\pi\sigma^2\rho)](1 - K + \dots), \quad (1b)$$

$$\lambda_{tr} = \frac{1}{4}\eta(k/m)(1 - \frac{1}{2}K + \dots), \quad (1c)$$

$$\lambda_{int} = \frac{9}{8}\eta(k/m)(1 + \frac{9}{4}K + \dots), \quad (1d)$$

$$\tau^{-1} = \frac{1}{3}[\pi\sigma^2 p/(\pi mkT)^{1/2}](K + \dots), \quad (1e)$$

where $\rho = nm$ is the gas density and $p = nkT$ is the gas pressure. The approximate theory makes no evaluation of τ , but expresses its corrections in terms of τ and then uses Eq. (1e) to express these in terms of K . The approximate theory then gives no correction to η and D_{11} to first order in K . This is not so serious for η , but represents a rather large error in D_{11} . The approximate theory yields the correct value for λ_{tr} , but for λ_{int} it yields a correction term of $\frac{1}{2}K$ instead of $\frac{9}{4}K$, an error of over a factor of 2.

The rough-sphere model has a physically unrealistic feature that has been pointed out by Chapman and Cowling.⁷ Glancing or grazing collisions for this model do not, in general, produce a small deflection in the trajectories of the colliding pair, as in most other models, but can produce large deflections if the rotational velocities of the spheres are suitable. Averaged over many collisions with many initial angular veloci-

ties, this effect gives rise to an excess of backward scattering which appears to be primarily responsible for the discrepancy in D_{11} . Similarly, the roughness of the sphere gives rise to an excess of sideward scattering on the average (i.e., scattering around 90° in the center-of-mass system). This does not affect D_{11} , but both the backward and sideward scattering affect η . They do so in opposite directions, however, and so the net effect in η is small. In other words, rough spheres are better scatterers than smooth spheres, since they scatter more at 90° and 180° than do smooth spheres. On the other hand, real molecules are usually poorer scatterers than smooth spheres, since they scatter more in the forward direction.

Related to the more efficient scattering of rough spheres is another effect which does not seem to have been noticed before: Averaged over many rotational states, a certain fraction of collisions appear to occur as if a resonant exchange of internal energy took place. That is, it is as if two molecules sometimes collide with no change in the magnitude of the relative velocity of translation, but with an exchange of purely rotational energy. Resonant exchange effects have been observed for polar molecules which have long-range dipole forces. It is possible that they occur for nonpolar molecules too, but the effect is probably negligible.

We wish to emphasize that the above interpretations, which are set forth in more detail in the following section, are analogies that are valid only in an average sense, when all collisions are considered. They are certainly not true for individual collisions.

II. FORMULAS AND CALCULATIONS

In this section we evaluate the transport coefficients for the rough-sphere gas from the general formal kinetic theory of Wang Chang and Uhlenbeck and of Taxman. In this way we can investigate individual terms, neglected or approximated by Mason and Monchick, to gain some insight into their physical foundations.

We first write the general formulas in Wang and Uhlenbeck's semiclassical form, with the understanding that the summations over internal energy states are to be replaced by integrations over angular velocities. The formulas are expressed in terms of a collision between two molecules initially in internal energy states i and j , which are scattered (in the center-of-mass system) through a polar deflection angle χ and azimuthal angle α , and end up in internal states k and l . The differential cross section for this process is I_{ijkl} , which is a function of χ , α and the initial relative speed g . The relaxation time τ is

$$\tau^{-1} = (2nk/c_{int})(kT/\pi m)^{1/2} Q_{int}^{-2} \sum_{ijkl} \int (\Delta\epsilon)^2 d\Omega, \quad (2)$$

where n is the number density, $c_{int} = \frac{3}{2}k$ is the internal

⁶ F. B. Pidduck, Proc. Roy. Soc. (London) A101, 101 (1922).

⁷ Reference 3, Chap. 11.

⁸ M. Kohler, Z. Physik 124, 757 (1947); 125, 715 (1949). See also reference 3, pp. 396-398.

heat capacity per molecule, and

$$Q_{\text{int}} = \sum_i \exp(-\epsilon_i), \quad (3)$$

$$d\Omega = \exp(-\gamma^2 - \epsilon_i - \epsilon_j) \gamma^3 I_{ij}^{kl} \sin\chi d\chi d\alpha d\gamma, \quad (4)$$

in which ϵ_i is the internal energy of the i th internal state divided by kT , $\gamma^2 = mg^2/(4kT)$, and $\Delta\epsilon = \epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j$. The self-diffusion coefficient D_{11} , is⁹

$$D_{11}^{-1} = \frac{8}{3} \rho (\pi m k T)^{-1} Q_{\text{int}}^{-2} \sum_{ijkl} \int (\gamma^2 - \gamma\gamma' \cos\chi) d\Omega, \quad (5)$$

where γ' refers to the relative velocity after collision. The formula given in reference 5 differs by the replacement of γ' by γ . The coefficient of shear viscosity η is

$$\eta^{-1} = \frac{8}{3} (\pi m k T)^{-1} Q_{\text{int}}^{-2} \sum_{ijkl} \int [\gamma^4 \sin^2\chi + (\Delta\epsilon)^2 (\frac{1}{3} - \frac{1}{2} \sin^2\chi)] d\Omega. \quad (6)$$

The two coefficients of heat conduction are more complicated:

$$\lambda_{\text{tr}} [1 - Y^2/(XZ)] = 75k^2T/(8mX) + 15kTc_{\text{int}}Y/(4mXZ), \quad (7)$$

$$\lambda_{\text{int}} [1 - Y^2/(XZ)] = \frac{3}{2} c_{\text{int}}^2 T/(mZ) + 15kTc_{\text{int}}Y/(4mXZ). \quad (8)$$

The integrals X , Y , and Z are rather complicated, but X and Y can be written *without approximation* in terms of τ and η , as follows⁵:

$$X = 5kT/(2\eta) + 25c_{\text{int}}/(12nkr), \quad (9)$$

$$Y = 5c_{\text{int}}/(4nkr). \quad (10)$$

The integral Z is more difficult, and approximations must be made in order to express it in terms of measurable quantities.⁵ The exact expression is

$$Z = 4(kT/\pi m)^{1/2} Q_{\text{int}}^{-2} \sum_{ijkl} \int (\epsilon_i - \bar{\epsilon}) [-\frac{3}{2}\Delta\epsilon + \gamma^2(\epsilon_i - \epsilon_j) - \gamma\gamma'(\epsilon_k - \epsilon_l) \cos\chi] d\Omega, \quad (11)$$

where

$$\bar{\epsilon} = Q_{\text{int}}^{-1} \sum_i \epsilon_i \exp(-\epsilon_i). \quad (12)$$

As far as heat conduction is concerned, the integral Z is the heart of the problem. By a series of arguments Z was previously given by⁵

$$Z \approx \frac{3}{2} [c_{\text{int}}T/(\rho D_{\text{int}})] + \frac{3}{4} [c_{\text{int}}/(nkr)], \quad (13)$$

where D_{int} was essentially the diffusion coefficient for internal energy. For rough spheres, the same arguments that led to Eq. (13) lead to $D_{\text{int}} \approx D_{11}$ (smooth

sphere); i.e., to the expression given in Eq. (1b), but with the correction term in K absent. Specifically, the terms in γ' and $\cos\chi$ may be expanded in series in $\Delta\epsilon$. We note that all terms multiplied by $\cos\chi$ (smooth sphere), the zeroth approximation to $\cos\chi$, vanish when integrated over all angles. Therefore, the deviation, if any, from the smooth-sphere result must come from the dependence of the deflection angle χ on inelastic collisions. This is confirmed for the rough-sphere case by an exact calculation.

The formulas above already make clear why the approximate theory gave λ_{tr} correct to first order in K , but not λ_{int} . In Eq. (7) for λ_{tr} , the only approximations necessary involve Z , but since this occurs in a term already first order in K (because of the presence of Y), a zeroth-order approximation for Z suffices to give λ_{tr} correct to first order. However, for λ_{int} , the first term on the right of Eq. (8) must be evaluated correct to first order in K , and so an approximation for Z accurate to first order is necessary.

To proceed further with the analysis it is necessary to consider the collision dynamics for rough spheres. Let the initial internal states i and j of the two colliding molecules be represented by the angular velocities ω_1 and ω_2 , respectively, and the final states k and l by ω_1' and ω_2' . That is,

$$\epsilon_i = \frac{1}{2} I \omega_1^2 = K m \sigma^2 \omega_1^2 / (8kT), \quad (14)$$

with similar expressions for ϵ_j , ϵ_k , and ϵ_l . Conservation of energy and momentum give for the deflection angle χ the expression

$$\begin{aligned} \mathbf{g} \cdot \mathbf{g}' &= gg' \cos\chi \\ &= g^2 - 2(1+K)^{-1} (\mathbf{g} \cdot \mathbf{k})^2 \\ &\quad - K(1+K)^{-1} [2g^2 - \sigma(\mathbf{g} \cdot \mathbf{k} \times \boldsymbol{\omega})], \end{aligned} \quad (15)$$

where \mathbf{g} and \mathbf{g}' are the relative velocities before and after collision, respectively, \mathbf{k} is the unit vector in the direction of the line connecting the centers of the spheres at impact, and $\boldsymbol{\omega} = \omega_1 + \omega_2$. For smooth spheres ($K=0$) the term in brackets vanishes, and $\mathbf{g} \cdot \mathbf{k} = g \cos(\frac{1}{2}\pi - \frac{1}{2}\chi)$, from which follows the well-known result, $g' = g$. The change in internal energy on collision is given by

$$\begin{aligned} \Delta\epsilon &= \gamma^2 - \gamma'^2 \\ &= K(1+K)^{-2} (m/kT) [g^2 - (\mathbf{g} \cdot \mathbf{k})^2 - \frac{1}{2}\sigma(1-K) \\ &\quad \times (\mathbf{g} \cdot \mathbf{k} \times \boldsymbol{\omega}) - \frac{1}{4}\sigma^2 K (\mathbf{k} \times \boldsymbol{\omega})^2], \end{aligned} \quad (16)$$

which of course is zero for smooth spheres. All other relations needed can be obtained from Eqs. (15) and (16) by algebraic manipulation. The integrations over trajectories and internal states are best carried out using the coordinate system suggested by Kohler.⁸ Let the angle between \mathbf{g} and \mathbf{k} be ψ , that between $\boldsymbol{\omega}$ and \mathbf{k} be θ , and that between the planes determined by \mathbf{g}

⁹ L. Monchick, K. S. Yun, and E. A. Mason (to be published).

and \mathbf{k} and by \mathbf{k} and $(\mathbf{k} \times \boldsymbol{\omega})$ be ϕ . The angle between \mathbf{g} and \mathbf{g}' is as always χ . Then we find

$$\begin{aligned} I_{ij}^{kl} \sin \chi d\chi d\alpha &= \sigma^2 \sin \psi d\psi d\alpha, \\ \mathbf{g} \cdot \mathbf{k} &= g \cos \psi, \\ |\mathbf{k} \times \boldsymbol{\omega}| &= \omega \sin \theta, \\ \mathbf{g} \cdot \mathbf{k} \times \boldsymbol{\omega} &= -g\omega \sin \psi \sin \theta \cos \phi. \end{aligned} \quad (17)$$

The first expression in (17) depends on the fact that \mathbf{g} , $\boldsymbol{\omega}_1$, and $\boldsymbol{\omega}_2$ uniquely determine \mathbf{g}' , $\boldsymbol{\omega}_1'$, and $\boldsymbol{\omega}_2'$, so that the expression is valid provided the integrations over trajectories (i.e., over χ and ϕ or over ψ and ϕ) are carried out at fixed values of \mathbf{g} , $\boldsymbol{\omega}_1$, and $\boldsymbol{\omega}_2$. Because of this the summation over internal states can be replaced by an integration over $d\boldsymbol{\omega}_1$ and $d\boldsymbol{\omega}_2$. If we let $\boldsymbol{\omega}_2 + \boldsymbol{\omega}_1 = \boldsymbol{\omega}$ and $\boldsymbol{\omega}_2 - \boldsymbol{\omega}_1 = 2\mathbf{v}$, then $d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 = d\boldsymbol{\omega} d\mathbf{v}$, and

$$\begin{aligned} d\boldsymbol{\omega} &= \omega^2 d\omega \sin \theta d\theta d\phi, \\ d\mathbf{v} &= v^2 dv \sin \theta' d\theta' d\phi', \end{aligned} \quad (18)$$

where θ' and ϕ' are defined analogously to θ and ϕ . The integrations in Eqs. (3) and (4) become

$$\begin{aligned} Q_{\text{int}} &= (I/2\pi)^{\frac{1}{2}}, \\ \sum_{ijkl} \int \cdots d\Omega &= \int_0^\infty d\gamma \gamma^3 \exp(-\gamma^2) \int_0^{\pi/2} d\psi \sigma^2 \sin \psi \cos \psi \int_0^{2\pi} d\alpha \\ &\times \int_0^\infty d\omega \omega^2 \exp(-I\omega^2/4) \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \\ &\times \int_0^\infty dv v^2 \exp(-Iv^2) \int_0^\pi d\theta' \sin \theta' \int_0^{2\pi} d\phi'. \end{aligned} \quad (19)$$

The integrations in Eqs. (2), (5), (6), and (11) can now be carried out in straightforward fashion.

Let us first consider the integration in Eq. (5), which determines D_{11} . This involves the integral

$$Q_{\text{int}}^{-2} \sum_{ijkl} \int (\gamma^2 - \gamma\gamma' \cos \chi) d\Omega \equiv \langle \gamma^2 - \gamma\gamma' \cos \chi \rangle, \quad (21)$$

which, on substitution from Eq. (15) for $\gamma\gamma' \cos \chi$, yields

$$\begin{aligned} \langle \gamma^2 - \gamma\gamma' \cos \chi \rangle &= (1+K)^{-1} \langle (\boldsymbol{\gamma} \cdot \mathbf{k})^2 + 2K\gamma^2 \rangle \\ &= (1+K)^{-1} (1+2K) \langle \gamma^2 \rangle, \end{aligned} \quad (22)$$

the term in $(\boldsymbol{\gamma} \cdot \mathbf{k} \times \boldsymbol{\omega})$ from (15) going to zero because of the integration over ϕ and θ which is equivalent to a sum over all directions of the vectors $\boldsymbol{\omega}$ and \mathbf{v} . The term $(\boldsymbol{\gamma} \cdot \mathbf{k})^2$ in Eq. (22) is the smooth-sphere term, and in fact gives the same value for both smooth and rough spheres on carrying out the integrations. For rough spheres, however, it is reduced by the factor $(1+K)^{-1}$ appearing in (22). The term $K\gamma^2$ represents just the extra backward scattering due to the roughness of the spheres, since the extra sideward scattering con-

tributes nothing to $\cos \chi$. It may be verified from this that to first order in K , γ' may be replaced by γ , as was suggested by the approximate model of Mason and Monchick. This suggests an analogous model in which all collisions are elastic, but a fraction f_π have an excess backward scattered component over smooth-sphere scattering and a fraction $f_{\pi/2}$ have an excess sideward component. The fraction $(1-f_{\pi/2}-f_\pi)$ represents specular scattering (smooth-sphere collisions). We can then easily compute the correction for D_{11} as follows:

$$\begin{aligned} \langle \gamma^2 - \gamma\gamma' \cos \chi \rangle &= (1-f_{\pi/2}-f_\pi) \langle \gamma^2 (1 - \cos \chi) \rangle_s \\ &+ f_{\pi/2} \langle \gamma^2 (1 - \cos \chi) \rangle_{\pi/2} + f_\pi \langle \gamma^2 (1 - \cos \chi) \rangle_\pi, \end{aligned} \quad (23)$$

where the subscript s refers to specular or smooth-sphere scattering, and the subscripts π and $\pi/2$ refer to backward and sideward scattering, respectively. It is well known that $\langle \cos \chi \rangle_s = 0$, and if we set $\langle \cos \chi \rangle_{\pi/2} = 0$ and $\langle \cos \chi \rangle_\pi = -1$, then Eq. (23) becomes

$$\langle \gamma^2 - \gamma\gamma' \cos \chi \rangle = [(1-f_\pi) + 2f_\pi] \langle \gamma^2 \rangle, \quad (24)$$

the first term in brackets representing the specular and sideward scattering contributions, and the second term representing the backward scattering. (The sideward scattering actually contributes nothing and could have been left out of the discussions.) Comparing these terms with the corresponding terms of Eq. (22) we find that both terms give the result $f_\pi = K(1+K)^{-1}$. The fact that both terms yield the same value of f_π indicates that this simple model is self-consistent. This result is valid to all orders of K , not just first order, to avoid the difficulty of "fractions" becoming greater than unity for large K .

A similar result holds for the viscosity, which involves the integral

$$\langle \gamma^4 \sin^2 \chi + \frac{1}{3} (\Delta \epsilon)^2 - \frac{1}{2} (\Delta \epsilon)^2 \sin^2 \chi \rangle. \quad (25)$$

To first order in K , the two terms involving $(\Delta \epsilon)^2$ cancel when the integrations are carried out. It is easy to see why this happens in terms of our simplified model of specular scattering plus excess backward and sideward scattering. The terms in $(\Delta \epsilon)^2$ must always be first order in K ; so that to evaluate $\langle \Delta \epsilon^2 \sin^2 \chi \rangle$ to first order in K , we may write it $\langle (\Delta \epsilon)^2 \rangle \langle \sin^2 \chi \rangle$ and use a zeroth order approximation for $\langle \sin^2 \chi \rangle$, namely the specular result, $\langle \sin^2 \chi \rangle_s = \frac{2}{3}$. Thus the two terms involving $(\Delta \epsilon)^2$ cancel to these approximations.

Introducing the simplified model again, with $f_{\pi/2}$ and f_π denoting the fraction of excess sideward and backward scattering, the integral (25) becomes

$$\begin{aligned} \langle \gamma^4 \sin^2 \chi \rangle &= (1-f_{\pi/2}-f_\pi) \langle \gamma^4 \sin^2 \chi \rangle_s + f_{\pi/2} \langle \gamma^4 \sin^2 \chi \rangle_{\pi/2} \\ &+ f_\pi \langle \gamma^4 \sin^2 \chi \rangle_\pi. \end{aligned} \quad (26)$$

Since $\langle \sin^2 \chi \rangle_s = \frac{2}{3} \langle \sin^2 \chi \rangle_{\pi/2} = 1$, and $\langle \sin^2 \chi \rangle_\pi = 0$, we see that the excess backward scattering decreases the cross

section (increases the viscosity) and the excess side-ward scattering increases the cross section (decreases the viscosity). The latter effect dominates, but the net effect is small since the exact correction factor to the cross section is known to be^{6,7} $(1 + \frac{1}{6}K)(1+K)^{-2} = 1 + \frac{1}{6}K + \dots$. Comparing this with Eq. (26) and using our previous result, $f_{\pi} = K(1+K)^{-1}$, we find that $f_{\pi/2} = \frac{1}{3}K(1+K)^{-2}$, where we have kept higher orders of K only to avoid "fractions" greater than unity. (The analogy for η is not exact to higher orders in K , unlike that for D_{11} , because we have suppressed the term in $(\Delta\epsilon)^2$.)

Lest our analogy seem too arbitrary, it should be remembered that the scattering cross section may always be analyzed into a smooth-sphere scattering term plus a deviation. The deviation may be analyzed into components which have maxima at given angles χ . Since we have supposed that only two moments of $\cos\chi$ are available, we may only analyze the deviation into two components. This is allowable in the rough-sphere case since, as we have seen, the deviations from the approximate formulas of Mason and Monchick⁵ come, to first order in K , not from terms involving powers of γ' and $\Delta\epsilon$, but from the deviation of the deflection angle χ from the smooth-sphere value. The analogy proposed here is also only a first-order model since we have supposed all collisions elastic, e.g., $\gamma' = \gamma$.

Finally, we consider the integral Z , which determines λ_{int} . In the expression for Z given in Eq. (11), the term in $\Delta\epsilon$ can be converted to a term in $(\Delta\epsilon)^2$ and hence to τ by permuting variables.⁵ Hence no approximation is involved in evaluating this term. The crucial part of Z is thus the integral

$$\langle (\epsilon_i - \bar{\epsilon}) [(\epsilon_i - \epsilon_j)\gamma^2 - (\epsilon_k - \epsilon_l)\gamma\gamma' \cos\chi] \rangle. \quad (27)$$

The part that is troublesome in (27) is the factor $(\epsilon_k - \epsilon_l)$, since this refers to internal states *after* collision. Converting to the rough-sphere system, we find that

$$(\epsilon_i - \epsilon_j)(\epsilon_k - \epsilon_l) = (mK\sigma^2/8kT)^2(\omega \cdot \mathbf{v}) \times [\omega \cdot \mathbf{v} - (2/\sigma)(1+K)^{-1}\mathbf{v} \cdot \mathbf{k} \times \mathbf{g} + (1+K)^{-1}\mathbf{v} \cdot \mathbf{k} \times \mathbf{k} \times \omega], \quad (28)$$

where

$$\mathbf{v} \cdot \mathbf{k} \times \mathbf{k} \times \omega = v\omega \cos\theta \cos\theta' - \omega \cdot \mathbf{v}. \quad (29)$$

On integrating over all directions of ω and \mathbf{v} we find that the term in $\mathbf{v} \cdot \mathbf{k} \times \mathbf{g}$ cancels the term in $v\omega \cos\theta \times \cos\theta'$, leaving finally

$$\langle (\epsilon_i - \epsilon_j)(\epsilon_i - \epsilon_j)[\gamma^2 - (K-1)(1+K)^{-1}\gamma\gamma' \cos\chi] \rangle. \quad (30)$$

The remaining integrations can be carried out to yield the result of Pidduck, which need not be reproduced here. We may now compare with the approximate formula,⁵

$$(c_{int}/k) \langle \gamma^2 - \gamma\gamma' \cos\chi \rangle. \quad (31)$$

The bracket expression in Eq. (31) is just proportional to the cross section for self-diffusion. It may be verified that Eq. (30) can be similarly reduced to

$$(c_{int}/k) \langle \gamma^2 - (K-1)(1+K)^{-1}\gamma\gamma' \cos\chi \rangle. \quad (32)$$

This is valid to all orders of K , and is strongly reminiscent of the expression derived by Mason and Monchick⁵ for the case when resonant collisions may occur. For this case two molecules exchange their internal energies without loss, so that $\epsilon_k = \epsilon_j$ and $\epsilon_l = \epsilon_i$, instead of $\epsilon_k = \epsilon_i$ and $\epsilon_l = \epsilon_j$ as for an elastic collision. If the probability of exchange is P_{ex} , then (27), which is general and is not restricted to the rough sphere case, can be written as

$$\begin{aligned} & \langle (\epsilon_i - \bar{\epsilon})(\epsilon_i - \epsilon_j)[P_{ex}(\gamma^2 + \gamma\gamma' \cos\chi) + (1 - P_{ex}) \\ & \quad \times (\gamma^2 - \gamma\gamma' \cos\chi)] \rangle = \langle (\epsilon_i - \bar{\epsilon})(\epsilon_i - \epsilon_j) \\ & \quad \times [\gamma^2 - (1 - 2P_{ex})\gamma\gamma' \cos\chi] \rangle. \quad (33) \end{aligned}$$

Equation (32) may be written in this form if we replace P_{ex} by $(1+K)^{-1}$, the value of P_{ex} coming entirely from the $\omega \cdot \mathbf{v}$ term of Eq. (29). However, the analogy is not complete. P_{ex} for rough spheres is not the probability of exchange, but the fraction of energy exchanged. Equation (32) states that for given values of ω , \mathbf{v} , and γ the quantity $\epsilon_i - \epsilon_j$ in the mean is multiplied by a factor of $(K-1)(1+K)^{-1}$ —in other words, that the internal energies of the two colliding molecules tend to equalize. For finite values of P_{ex} in the case of polar molecules, the region where $\chi \approx 0$ is heavily weighted and the net effect is to reduce the effective diffusion coefficient for the diffusion of internal energy. However, in the case of rough spheres, the scattering has a sizable backward scattering component. The net effect is to increase the internal diffusion coefficient. This latter effect is not born out by experiment with the possible exception of hydrogen at high temperatures.⁵ However, the anomalous hydrogen result may be due to some concealed experimental error.

III. DISCUSSION

In summary, we have shown that the peculiar transport properties of a rough-sphere gas can be understood in first approximation as the result of two effects: (1) an enhancement of the backward and sideward scattering over that for smooth spheres; and (2) an apparent resonant exchange of internal energy on collision of two rough spheres, with a probability between 0.6 and 1.0. It is to be emphasized again that these effects are really only analogies that are true in an average sense. Since molecules interact with potentials that tail off more slowly than the hard-sphere potential, (1) is probably a property only of rough spheres with the possible exception of H_2 . (2) may be a more widespread property (as is the case, for instance, for polar mole-

cules⁵) but since the scattering for real molecules probably has less of a backward scattered component the net effect is generally to decrease the thermal conductivity rather than to increase it. Since the effects are, for the most part, peculiar to rough spheres and are not expected to operate for most real molecules, we believe that the present results support the view that the discrepancies between the exact rough-sphere results and the approximate theory of Mason and

Monchick are due to the special properties of the rough sphere model.

As an incidental result, we have verified that the formal kinetic theory of Wang Chang and Uhlenbeck and of Taxman does yield the known results for rough spheres, which were derived by a more specialized method. While this result is hardly surprising, it at least indicates that no serious errors exist in the formal kinetic theory expressions.